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(54) **Vapor phase hydrogenation of carbon tetrachloride.**

(57) A vapor phase process for the hydrodechlorination of carbon tetrachloride to produce chloroform and methylene chloride utilizes a supported platinum catalyst that is subjected to chloride pre-treatment. The platinum catalyst may be promoted with small amounts of metals such as tin and titanium. By-product production is decreased and duration of catalyst activity is improved by the process of this invention.

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This invention is related to the vapor phase hydrogenation of carbon tetrachloride to form chloroform and methylene chloride.

Various methods of dehalogenating saturated and unsaturated organic compounds are known. For example, U.S. Patent 3,579,596, issued to Mullin et al. on May 18, 1971, is directed to the vapor phase dechlorination of carbon tetrachloride and/or chloroform in the presence of a platinum catalyst. The hydrodechlorination of carbon tetrachloride with hydrogen over peripherally deposited platinum on alumina is also discussed by Weiss et al. in *Journal of Catalysis* 22, 245-254 (1971). However, as discussed by Noelke and Rase in *Ind. Eng. Chem. Prod. Res. Dev.* 18, 325-328 (1979), such processes have been marked with poor selectivity, rapidly declining catalyst activity and short reactor operating cycles. Various treatments have been explored to improve activity and selectivity. These include pretreating catalysts with sulfur and hydrogen.

This invention is a vapor phase process for the catalytic hydrogenation of carbon tetrachloride to produce chloroform and methylene chloride by the reaction of carbon tetrachloride and hydrogen characterized by the use of a catalyst selected from the group consisting of

- (1) a supported platinum group metal catalyst pretreated by exposure to a chloride source prior to contact with the carbon tetrachloride and hydrogen;
- (2) a supported platinum group metal catalyst further comprising at least one component selected from tin, rhenium, germanium, titanium, lead, silicon, phosphorus, arsenic, antimony, bismuth or mixtures thereof; and
- (3) a supported platinum group metal catalyst further comprising at least one component selected from tin, rhenium, germanium, titanium, lead, silicon, phosphorus, arsenic, antimony, bismuth or mixtures thereof pretreated by exposure to a chloride source prior to contact with the carbon tetrachloride and hydrogen;

under conditions sufficient to form chloroform and methylene chloride.

This process reduces the production of by-products such as hexachloroethane, perchloroethylene and methane; maintains the carbon tetrachloride conversion level relatively constant; and results in a low rate of catalyst deactivation.

The carbon tetrachloride and hydrogen are contacted at any temperature and pressure at which the desired hydrodechlorination will occur. It is preferred that the temperature is at least about 50°C and no greater than about 200°C; more preferred that the temperature is at least about 75°C and no greater than about 150°C; and most preferred that the temperature is at least about 80°C and no greater than about 130°C. The pressure is preferred to be at least about atmospheric and no greater than about 1500 kPa; more preferred that the pressure is about 200 kPa and no greater than about 1100 kPa; and most preferred that the pressure is at least 275 kPa and no greater than 800 kPa. It will be recognized by one skilled in the art that higher temperatures and pressures are operable in the practice of this invention, but may not be preferred due to economic or other considerations. The process may be conducted in a batch or continuous manner.

Hydrogen and carbon tetrachloride are typically reacted to form chloroform and methylene chloride. In some preferred embodiments, hydrogen chloride is also included in the reactant feed. Any amounts of hydrogen, carbon tetrachloride and, optionally, hydrogen chloride which will result in the formation of chloroform and methylene chloride at an acceptable yield are useful in the practice of this invention. Preferably the mole ratio of hydrogen to carbon tetrachloride ranges from 1:1 to 30:1; more preferably from 2:1 to 12:1 and even more preferably from 3:1 to 9:1. The mole ratio of carbon tetrachloride to hydrogen chloride ranges from 1:0 to 1:6; more preferably from 1:1 to 1:2. The upper limit on the amount of hydrogen chloride present in the reactant feed is related to catalyst activity. The activity of the catalyst, as determined by carbon tetrachloride conversion, appears to decrease as the amount of hydrogen chloride in the reactant feed increases. However, selectivity to chloroform increases as the amount of hydrogen chloride in the reactant feed increases. Thus, one skilled in the art will recognize that the optimum amount of hydrogen chloride to be included in the reactant feed will be selected to balance conversion of carbon tetrachloride and selectivity to chloroform. In reaction schemes wherein it is feasible to recycle significant amounts of carbon tetrachloride, the selectivity to chloroform obtained by higher amounts of hydrogen chloride may outweigh loss of conversion of carbon tetrachloride.

Platinum group metal catalysts are useful in this invention. By platinum group metal is meant ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof. The catalyst will preferably contain platinum. The catalyst, in certain preferred embodiments, will also contain a second metal component selected from tin, titanium, germanium, rhenium, silicon, lead, phosphorus, arsenic, antimony, bismuth or mixtures thereof. It is preferred that the catalyst contain platinum and at least one of tin, titanium or germanium.

The amount of platinum group metal present in the catalyst is preferably at least 0.01 weight percent based on the weight of the total catalyst and no greater than 5.0 weight percent. Preferred ranges are from 0.03 weight percent to 0.5 weight percent.

The second metal, when present, is preferably present in a weight ratio of platinum group metal to second metal of from 500:1 to 2:1. The ratio is more preferably from 200:1 to 10:1.

The catalyst of the present invention is preferably supported. The support is preferably a porous, adsorptive, high-surface area support having a surface area of 25 to 500 square meters per gram. Examples of suitable support materials include activated carbon, coke or charcoal; silica or silica gel, silicon carbide, clays and silicates including those synthetically prepared and naturally occurring, which may or may not be acid treated, for example attapulgus clay, diatomaceous earth, fuller's earth, kaoline, kieselguhr; inorganic oxides such as alumina, titanium dioxide, zirconium dioxide, chromium oxide, zinc oxide, magnesia, thoria, boria, silica-alumina, silica-zirconia, silica-magnesia, chromia-alumina; crystalline zeolitic aluminosilicates; and combinations of one or more elements from one or more of these groups. Alumina supports are preferred for the catalysts of the present invention.

Preferred supports have surface areas ranging from 50 to 350 m<sup>2</sup>/gm, more preferably from 80 to 250 m<sup>2</sup>/gm. The average pore diameter of the preferred support ranges from 25 to 200 angstroms, more preferably from 50 to 125 angstroms. The average diameter of the catalyst is from 1.5 to 12.5 mm.

The platinum group metal and second metal may be incorporated into the catalyst support in any suitable manner. Examples of suitable techniques include precipitation, ion-exchange or impregnation. The metals may be incorporated into the support at the same time or may be incorporated separately. In a preferred embodiment, the platinum group metal and second metals are incorporated separately.

The method of incorporation into the support is one variable which affects the distribution of the metal on the support. In the practice of the present invention, the platinum group metal may be distributed on the surface of the catalyst support or it may be distributed on or within the support. By distribution of the metal on or within the support, it is meant the distance from the surface of the support that the metal or metals penetrate measured in microns. It is preferred that the platinum group metal is distributed at least 50 microns and no greater than 650 microns from the surface and more preferred that it is distributed at least 250 microns and no greater than 350 microns from the surface.

Like the platinum group metal, the second metal may be located on the surface of the support or it may be distributed on or within the support. It is preferred that the second metal is distributed at least 100 microns and no greater than 1000 microns from the surface. It is more preferred the the second metal is distributed at least 300 microns and no greater than 500 microns from the surface.

In addition to the platinum group metal and the second metal, the catalyst may contain other components such as alkali metal, alkaline metal, halogen, sulfur and other known catalyst modifiers.

The catalysts useful in this invention may be purchased commercially. An example is a platinum on alumina catalyst. The catalysts may also be prepared by methods known in the art. For example, U.S. Patent 4,786,625 to Imai et al, issued November 22, 1988, describes a catalyst comprising a platinum group metal component, a modifier metal component selected from group consisting of tin, germanium, rhenium and mixtures thereof on a refractory oxide support having a nominal diameter of at least about 850 microns wherein the platinum group metal component is surface impregnated such that the average concentration of the surface-impregnated platinum group component on the outside 100 micron layer of the catalyst is at least 2 times the concentration of the platinum group component in the 200 micron diameter center core of the catalyst and wherein the modifier metal component is uniformly impregnated through the refractory oxide support and a method of making such a catalyst.

Prior to being used in the process of the present invention, the catalyst is preferably pretreated with a chloride source. In one preferred embodiment, the catalyst is subjected to a multi-step pre-treatment comprising drying the catalyst, reducing the catalyst, and subjecting the catalyst to at least two treatments with a chloride source wherein a later treatment or treatments with the chloride source is conducted at a temperature lower than that used in an earlier treatment.

For example, in one preferred embodiment, the catalyst is subjected to a pre-treatment comprising the following steps:

- (1) drying the catalyst under an diluent gas at an elevated temperature;
- (2) treating the catalyst with a chloride source selected from the group comprising hydrochloric acid and chlorine at an elevated temperature;
- (3) reducing the catalyst; and
- (4) treating the catalyst a second time with a chloride source selected from the group comprising hydrochloric acid and chlorine at a temperature less than the temperature used in step (2).

In the drying step, it is preferred that the diluent gas is nitrogen. The temperature is preferably from

100 °C to 500 °C. The time required for the drying step is preferably from two hours to six hours.

In the first chloride treatment, the chloride source with which the catalyst is treated is preferably hydrochloric acid. The temperature in this step of the pre-treatment is preferably from 150 °C to 300 °C. The time required for this step is preferably from two hours to four hours.

5 In the reduction, the catalyst is reduced using a conventional reducing agent. Examples of suitable reducing agents include hydrogen, hydrazine and formaldehyde. The reducing agent is preferably hydrogen. The temperature in this step of the pre-treatment is preferably from 150 °C to 500 °C. The time required for this step is preferably from two hours to twenty-four hours. As will be recognized by one skilled in the art, preferred temperatures and times are related so that at higher temperatures, less time will be  
10 required and at lower temperatures, more time will be required. The catalyst is cooled after this step, preferably to a temperature from about 80 °C to 150 °C.

In the second chloriding treatment, the chloride source with which the catalyst is treated is preferably hydrochloric acid. The temperature in this step of the pre-treatment is preferably about 80 °C to 150 °C, provided that the temperature used is less than that used in Step (2). The time required for this step is  
15 preferably from fifteen minutes to two hours.

The order of the various parts of the pre-treatment may be varied and in some cases steps will overlap. For example, the catalyst may be treated with a diluent gas and a chloride source at elevated temperatures simultaneously or the treatment with the inert gas and the chloride source may overlap for some period of time.

20 The following examples are provided to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are by weight.

#### Example 1 Preparation of Titanium Promoted Catalyst

25 A 0.266 g portion of  $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$  and 0.1180 g of  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$  were dissolved in the incipient wetness volume of 15.0  $\text{cm}^3$   $1.0 \times 10^{-2}$  N HCl and added to 20 grams of alumina having a surface area of 200  $\text{m}^2/\text{g}$  producing a catalyst containing 0.5 weight percent platinum and 0.1 weight percent titanium. The catalyst was air dried at ambient temperature for 12 hours. The catalyst was then calcined in air at 400 °C for four hours. The calcined catalyst was then reduced in a mixture of 10 percent hydrogen in nitrogen  
30 starting at 25 °C. The temperature was then raised to 400 °C at 10 °C per minute and held there for two hours. The catalyst was cooled under the reducing medium to 25 °C, flushed with nitrogen and passivated by exposure to one percent oxygen in nitrogen.

#### Example 2 Preparation of Tin Promoted Catalyst

35 The procedure outlined in Example 1 was followed with the exception that 0.037 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was substituted for the  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$ .

#### Example 3 Sequential Impregnation

40 The procedure of Example 1 was followed to produce a tin promoted catalyst except that 0.037 gm  $\text{SnCl}_2$  was dissolved in 15.0 cc 1.0 M HCl and added to 20.00 gm of alumina. The alumina was air dried at ambient temperature for 12 hours and calcined in air at 400 °C for four hours. The catalyst was cooled to room temperature and then impregnated with 0.266 gm of  $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$  dissolved in 15.0  $\text{cm}^3$  of  $1.0 \times 10^{-2}$  M HCl solution. The drying, calcination and reduction procedures of Example 1 were then followed to  
45 produce the catalyst.

A phosphorus containing catalyst was prepared using phosphoric acid in the procedure described above.

A germanium containing catalyst was prepared as described above using a commercially obtained ICP  
50 (inductively coupled plasma) standard solution containing germanium.

#### Example 4 Hydrogenation Reaction

55 A 12.7 mm by 305 mm Hastelloy C reactor tube fitted with a concentric thermal well was charged with 5.0  $\text{cm}^3$  (3.1 g) of a catalyst prepared in Example 1 (Runs 1-4), Example 2 (Runs 5-6) or Example 3 (Runs 7-9). The reactor was purged with  $\text{N}_2$  and HCl at a 10:1 molar ratio and a total gas flow of 200  $\text{cm}^3$  per minute. The pressure was maintained at 300 kPa by a research control valve. The reactor was heated to 100 °C and held for one hour. The reactor was temperature programmed to 200 °C and held for one hour.

The HCl flow was stopped and the reactor was cooled to 100°C under flowing N<sub>2</sub>. The N<sub>2</sub> was replaced with H<sub>2</sub> and the reactor was temperature programmed at 10°C per minute to 200°C and held there for two hours. The reactor was cooled to 100°C and the H<sub>2</sub> flow is set to 65 cm<sup>3</sup> per minute with a HCl flow of 2.5 cm<sup>3</sup> per minute. Vaporized CCl<sub>4</sub> was introduced at a liquid hourly space velocity (LHSV) of 0.5. Reaction products were monitored by on-line gas chromatography and the results are given in Table I below.

TABLE I

Run	Pt (ppm)	Second Metal	Second Metal (F) (ppm)⓪	Second Metal (U) (ppm)⓪	CH <sub>4</sub> (%)	Pt Profile (microns)	Temp exo/base °C	LHSV⓪
1	4500	Ti	23	--	14.9	150	109.6/100	0.5
2	4600	Ti	120	75	9.7	300	110/100	0.5
3	4500	Ti	560	310	8.2	300	105.8/100	0.5
4	4600	Ti	980	440	8.6	300	112.5/110	0.25
5	4500	Sn	580	448	7.0	450	100/90	0.5
6	4600	Sn	850	627	6.84	550	102/90	0.5
7	5000	Sn	890	750	5.45	450	95.5/90	0.5
8	4940	Ge	750	NA	8.3	400	84.5/80	0.5 (92.0%)
9	4600	P	150	NA	9.01	350	106/100	0.5 (99.1%)

⓪Content of Second Metal in Fresh catalyst

⓪Content of Second Metal in Used catalyst

⓪All conversions are 100% unless noted

In the following examples, a computer controlled apparatus constructed of a corrosion resistant nickel/copper alloy was used. The apparatus comprised two gas lines with one being fed by a cylinder of high purity hydrogen and the other being fed by a cylinder of electronic grade hydrogen chloride. Both were flow controlled by mass flow controllers to a common packed sample cylinder where the gasses were mixed and heated to 120°C by resistive heating. A high pressure syringe pump was used to meter carbon tetrachloride (CCl<sub>4</sub>) to another packed sample cylinder where it was vaporized and superheated to about 105°C by resistive heating. The two gas streams were mixed and fed to a reactor packed with 5 cm<sup>3</sup> of a commercially available catalyst (0.3 percent platinum on alumina). After passing over the catalyst, the effluent was transferred through a heated exit line to a gas sampling valve which injected a sample for gas chromatographic analysis. The bulk of the reactor effluent was then passed through a cold trap and then to a vent.

#### Comparative Example C-1

The process outlined above was followed. The catalyst was pre-treated by nitrogen drying at a temperature of about 200°C with a nitrogen flow of about 100 cm<sup>3</sup>/min for about two hours. The catalyst was then reduced by treatment with hydrogen at 200°C for about two hours before the reactant feed was started. The conversion of carbon tetrachloride and the ratio of methane to ethane were measured over time. The conversion of carbon tetrachloride was initially nearly 100 percent and then dropped to about 20 percent in about three hours and then gradually increased to about 85 percent after about 20 hours of run time. After fifty hours of run time, the conversion increased to over 90 percent. The methane to ethane ratio was near 100:1 at the beginning of the run time; dropped to about 8:1 after about two hours of run time; and then increased gradually to about 60:1. The methane to ethane ratio is related to catalyst deactivation with a higher ratio corresponding to a lower rate of deactivation. The primary products of this reaction were chloroform and methane. During the period of low carbon tetrachloride conversion, perchloroethylene and hexachlorethane were produced in significant quantities as identified by gas chromatography.

#### Comparative Example C-2

The general process and pre-treatment outlined in Example C-1 was followed with the exception that a 6:1 molar ratio of hydrogen to hydrogen chloride at 100°C was passed over the catalyst after it was dried and reduced. Following the treatment with hydrogen chloride, the catalyst was treated with pure hydrogen for thirty minutes at 100°C before the carbon tetrachloride flow was begun. The conversion of carbon tetrachloride started out near 100 percent and dropped to less than 10 percent within minutes of beginning the run and then gradually increased to about 90 percent after 200 hours of run time. The methane to ethane ratio reached only about 30:1 in this experiment.

#### Example 5 Effect of Chloride Soak

In this example, the catalyst was dried and then reduced with hydrogen as described in Example C-1. The catalyst was then exposed to pure hydrogen chloride at 100°C for one hour. Next a mixture of hydrogen chloride and hydrogen in a 1:1 molar ratio was passed over the catalyst for about 30 minutes at a temperature of about 100°C. Then carbon tetrachloride was added to the feed so that the molar ratio of hydrogen to carbon tetrachloride to hydrogen chloride was about 6:1:6. After about 15 minutes, the amount of hydrogen chloride was reduced so that the molar ratio of hydrogen to carbon tetrachloride to hydrogen chloride was about 6:1:1. The carbon tetrachloride conversion was relatively constant at about 98 percent. No drop in conversion is observed. No perchloroethylene or hexachloroethane are detected. The methane to ethane ratio quickly climbed to 80:1 and lined out at 100:1 to 120:1. The rate of catalyst deactivation is one percent loss of conversion per 300 hours of operation.

#### Example 6 High Temperature Hydrogen Chloride Treatment

In this example, the catalyst was dried under nitrogen at 200°C for four hours. It was then cooled to 100°C and pure hydrogen chloride was passed over the catalyst as the temperature was increased to 200°C and held there for two hours. The gas was then changed from pure hydrogen chloride to pure hydrogen and the temperature was maintained at 200°C for two hours. Next a mixture of hydrogen chloride and hydrogen in a 1:1 molar ratio was passed over the catalyst for 30 minutes at a temperature of 100°C. Then carbon tetrachloride was added to the feed so that the molar ratio of hydrogen to carbon tetrachloride

to hydrogen chloride was 6:1:6. After 15 minutes, the amount of hydrogen chloride was reduced so that the molar ratio of hydrogen to carbon tetrachloride to hydrogen chloride was 6:1:1. The conversion of carbon tetrachloride over time is 99.8 percent. A comparison of Examples 5 and 6 shows that treatment with hydrogen chloride at a high temperature (200°C) followed by a chloride soak at a lower temperature (100°C) results in a higher carbon tetrachloride conversion. The methane to ethane ratio ranges from 120:1 to 180:1. The rate of deactivation is estimated at 1 percent conversion loss per 2000 hours of operation.

#### Example 7 Reduction of Methane Production

The procedure of Example 5 was followed with the exception that the amount of hydrogen chloride in the reactant feed was varied from a ratio of 6:1:0 to 6:1:1 to 6:1:6,  $H_2:CCl_4:HCl$ . The conversion of carbon tetrachloride dropped from about 98.5 percent when the ratio was 6:1:0 to 90.5 percent when the ratio was 6:1:6. The selectivity to methane decreased from 25.5 percent when the ratio is 6:1:0 to 20.75 when the ratio was 6:1:6. A lower selectivity to methane indicates a higher selectivity to chloroform.

#### Claims

1. A vapor phase process for the catalytic hydrogenation of carbon tetrachloride to produce chloroform and methylene chloride by the reaction of carbon tetrachloride and hydrogen characterized by the use of a catalyst selected from the group consisting of
  - (1) a supported platinum group metal catalyst pretreated by exposure to a chloride source prior to contact with the carbon tetrachloride and hydrogen;
  - (2) a supported platinum group metal catalyst further comprising at least one component selected from tin, rhenium, germanium, titanium, lead, silicon, phosphorus, arsenic, antimony, bismuth or mixtures thereof; and
  - (3) a supported platinum group metal catalyst further comprising at least one component selected from tin, rhenium, germanium, titanium, lead, silicon, phosphorus, arsenic, antimony, bismuth or mixtures thereof pretreated by exposure to a chloride source prior to contact with the carbon tetrachloride and hydrogen;
 under conditions sufficient to form chloroform and methylene chloride.
2. The process of Claim 1 wherein the reactant feed further comprises hydrogen chloride.
3. The process of Claim 1 or 2 wherein the catalyst is a supported platinum group metal catalyst subjected to a pretreatment comprising exposing the catalyst to a chloride source.
4. The process of Claim 1 or 2 wherein the catalyst is a supported platinum group metal catalyst further comprising at least one component selected from tin, germanium, titanium or mixtures thereof.
5. The process of Claim 3 or 4 wherein the platinum group metal is platinum.
6. The process of Claim 1 or 2 wherein the pretreatment of the catalyst comprises at least two sequential treatments with a chloride source wherein a later treatment is conducted at temperature lower than that used in an earlier treatment.
7. The process of Claim 1 or 2 wherein the chloride source is hydrochloric acid.
8. The process of Claim 1 wherein the pretreatment of the catalyst comprises:
  - (1) drying the catalyst under an diluent gas at an elevated temperature;
  - (2) treating the catalyst with a chloride source selected from the group comprising hydrochloric acid and chlorine at an elevated temperature;
  - (3) reducing the catalyst; and
  - (4) treating the catalyst a second time with a chloride source selected from the group comprising hydrochloric acid and chlorine at a temperature less than the temperature used in step (2).
9. The process of Claim 1 or 2 wherein the reaction is conducted at a temperature range between about 50°C and 200°C.



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## EUROPEAN SEARCH REPORT

Application Number

EP 91 11 6390

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,D	INDUSTRIAL AND ENGINEERING CHEMISTRY, PRODUCT RESEARCH AND DEVELOPMENT vol. 18, no. 4, December 1979, WASHINGTON US pages 325 - 328; C.J. NOELKE: 'Improved hydrodechlorination catalysis: Chloroform over platinum-alumina with special treatments' * page 326, left column, paragraph 1 * * page 325, left column, paragraph 2 ** - - -	1,3,5,7,9	C 07 C 17/00 C 07 C 19/02 C 07 C 19/04
Y	WO-A-9 008 748 (DU PONT) * page 4, line 26 - page 5, line 7 ** - - -	1,5	
D,Y	US-A-3 579 596 (C. R. MULLIN ET AL.) * claims 1,2,4 ** - - -	1,5	
D,A	US-A-4 786 625 (T. IMAI) * abstract ** - - -	1	
A	CHEMICAL ABSTRACTS, vol. 111, no. 21, 20 November 1989, Columbus, Ohio, US; abstract no. 194097R, & JP-A-01-128942 (22.05.89) (ASAHI GLASS CO.): * abstract ** - - -	1	
A	EP-A-0 347 830 (ASAHI GLASS CO.) * page 3, line 38 - page 3, line 41 ** - - - - -	1	
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
Berlin		16 January 92	PROBERT C.L.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention		E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ..... &: member of the same patent family, corresponding document	